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Study of defect states in GaN films by photoconductivity measurement

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Optical absorption by defect states in gallium nitride (GaN) films was studied by photoconductivity (PC) spectroscopy at room temperature. A number of undoped *n*-type and Mg-doped *p*-type samples were employed in the present study. The PC response per absorbed photon decreased by more than four orders of magnitude as GaN became *p*-type conducting. Furthermore, all the samples exhibit PC response at photon energies far below the band gap energy of GaN. The optical absorption increases with photon energy $h\nu$ from 1.5 to 3.0 eV approximately as $\exp(h\nu/E_0)$. The parameter E_0 ranges from 180 to 280 meV, and is considerably smaller for the insulating *p*-type sample. For a *p*-type conducting sample, the PC response is flat between 0.7 and 1.4 eV. A model for the density of states distribution in the forbidden gap of GaN and the effect of Mg doping is proposed. © *1995 American Institute of Physics.*

Gallium nitride (GaN) is a potential candidate material for high temperature electronics and for blue-UV lasers. The defect states in the forbidden gap of GaN are usually characterized by luminescence measurements. Such measurements give information about defect states involved in radiative recombination processes, and thus cannot provide a full picture of the density of states distribution. The knowledge of the density of states distribution is critical in understanding the electronic transport and in optimizing device design and operation. For example, *p*-type conduction in GaN was recently achieved by magnesium (Mg) doping and proper post-deposition treatment.[1,2] Very little is known about the change in the density of states distribution when GaN becomes *p*-type conducting. A sensitive method for weak optical absorption measurement is the constant-photoconductivity (CPC) spectroscopy, popularly used in the study of hydrogenated amorphous silicon.[3,4] This technique should be applicable to GaN. Pankove and Berkeyheiser reported the PC spectra of Zn-doped GaN films grown by the chloride transport method.[5] We report here the PC spectra measurement on *n*-type and *p*-type GaN films grown by metalorganic chemical vapor deposition (MOCVD). The density of defect distribution in the forbidden gap of GaN seems to change drastically with Mg doping.

The undoped *n*-type and highly insulating *p*-type GaN thin films were grown on sapphire at Astralux in cold-wall low pressure MOCVD systems. Before deposition, the *R*-plane sapphire and basal plane sapphire substrates were degreased and cleaned in boiling phosphoric acid. The substrates were pretreated at 1050 °C in hydrogen. The triethylgallium (TEG) was transported into the reactor by hydrogen carrier gas. The ammonia flow rate was 500–1000 times that of the hydrogen carrier gas. The total pressure during deposition was 3 to 30 Torr. Mg doping was provided by transporting bis(cyclopentadienyl)magnesium (cp_2Mg) into the growth chamber with ammonia and TEG. The GaN films were grown at about 1030 °C on a GaN buffer layer deposited at about 500 °C. Our buffer layer growth conditions were not optimized. The deposited films are epitaxial wurtzitic GaN as shown by x-ray diffraction. The *p*-type conducting films were grown at Meijo University in Japan.

For the PC spectra measurement, a GE 1493 lamp was used as the light source. The radiation was filtered by a Perkin–Elmer model 12 monochromator equipped with a quartz prism. The photon flux versus photon energy at the specimen was separately measured by replacing the specimen with an RCA 31025 photomultiplier, a PbS detector, and a calibrated Si detector. Compared to a Xe arc lamp, the GE 1493 supplies much less UV light. As a result, the PC response of GaN remains within the same order of magnitude without the need to use attenuating neutral filters. The photoconductivity was measured in a coplanar geometry with two indium contacts soldered to the GaN surface. The *I–V* curve is linear for *n*-type samples, whereas for *p*-type films the *I–V* curve is linear for voltages greater than 0.3 V. A dc voltage (10 V for most of the measurement) was supplied to the sample through a series resistor. The voltage output from across either the sample or the load resistor, the one with the smaller resistance, was detected by the lock-in technique. The chopper frequency was 7 Hz. The PC signal decreases by a factor of 2 at a chopping frequency of about 20 Hz. For successful measurement, it is important to reduce the contact noise.

In this letter, the PC response is represented by $Y = \sigma_{\rm ph} d/eF$, where $\sigma_{\rm ph}$ is the photoconductivity corresponding to the incident flux F, d is the film thickness, and e is the electron charge. Thus,

$$Y = \sigma_{\rm ph} d/eF = (1-R)(1-e^{-\alpha d})[(\eta\mu\tau)_e + (\eta\mu\tau)_h],$$

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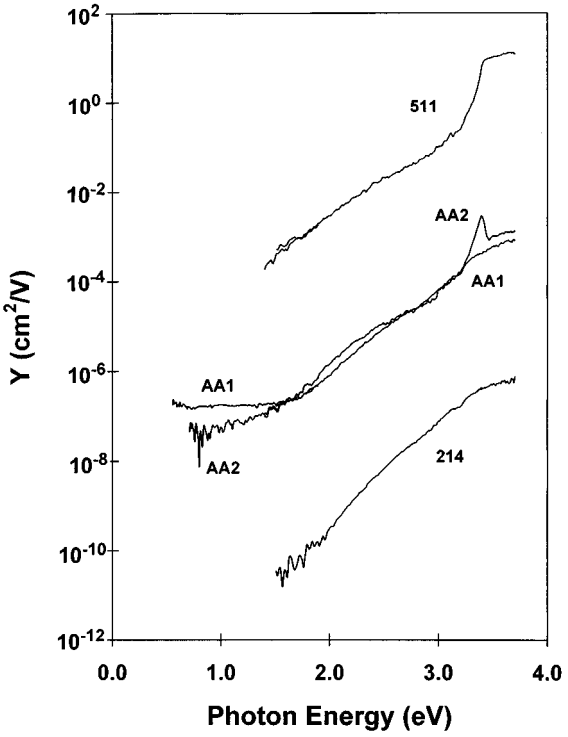

FIG. 1. PC spectra of several Mg-doped GaN films compared to the undoped *n*-type GaN sample 511.

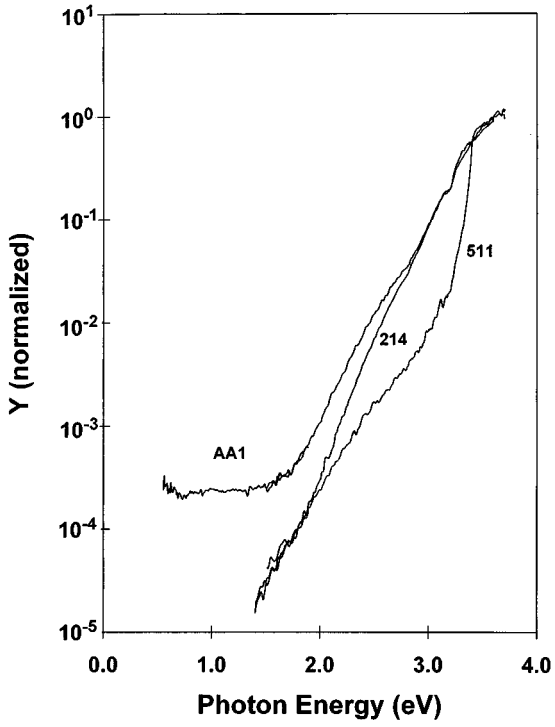

FIG. 2. Normalized PC spectra of a highly insulating *p*-type GaN film (sample 214), a *p*-type conducting GaN film (sample AA1, $p=6\times10^{17}$ cm^{-3} at 300 K), and an undoped GaN film (sample 511).

where R and α are, respectively, the reflection coefficient and the absorption coefficient for the incident light. The subscripts e and h represent, respectively, the contribution of photoexcited electrons and holes to the photoconductivity. η, μ, and τ are, respectively, the quantum efficiency for photogeneration, the mobility, and the lifetime of the photoexcited carriers.

The effect of Mg doping on the PC spectra is shown in Fig. 1. Sample 511 is undoped, exhibiting at room temperature a Hall mobility of 154 cm^2/V s, an electron concentration of 1.3×10^{18} cm^{-3}, and a strong near edge light emission. AA1 and AA2 are *p*-type conducting, with room temperature hole concentrations of 6×10^{17} cm^{-3} and 7×10^{16} cm^{-3}, respectively. Sample 214 is insulating *p* type. As a result of Mg doping, the PC response Y decreased by several orders of magnitude and decreased by nearly the same amount at any given photon energy. Since $1-e^{-\alpha d}\approx1$ for $h\nu>E_g$, the several orders of magnitude decrease in Y is attributable to a corresponding decrease in $(\eta\mu\tau)_e+(\eta\mu\tau)_h$.

For each sample, the photoconductivity at all photon energies is much lower than the dark conductivity. Thus, the lifetime of the majority carriers is approximately independent of the photon energy because of the extremely small variation of the quasi-Fermi level. For clarity of later discussion, we shall define here $r_n=(\eta\mu\tau)_e/[(\eta\mu\tau)_e+(\eta\mu\tau)_h]$ for the *n*-type sample and $r_p=(\eta\mu\tau)_h/[(\eta\mu\tau)_e+(\eta\mu\tau)_h]$ for the *p*-type sample to indicate the contribution of the majority carriers to PC. If we assume that electrons and holes excited to states within the forbidden gap are not mobile, photons with $h\nu$ several tenths of an eV less than E_g produce mostly mobile electrons in *n*-type GaN and mobile holes in *p*-type GaN. The PC spectra thus can be normalized to yield $1-e^{-\alpha d}$ for $h\nu>E_g$ and $r_n\alpha d$ (or $r_p\alpha d$ if *p* type) for $h\nu$ several tenths of an eV less than E_g, if R does not vary much with photon energy. We found that PC spectra measured with chopper frequencies of 5–160 Hz yield identical normalized spectra, supporting our assumption that the lifetime of the majority carriers is independent of photon energy. The PC spectra in Fig. 1 are normalized at 3.6 eV and replotted in Fig. 2, which shows that all the GaN films absorb light from near infrared to UV. The optical absorption increases with photon energy $h\nu$ from 1.5 to 3.0 eV approximately as $\exp(h\nu/E_0)$. E_0 for undoped *n*-type samples ranges from 230 to 280 meV. The E_0 parameter is 226 and 180 meV for sample AA1 and sample 214, respectively. Previous direct transmission measurements revealed an exponential absorption tail in the visible to near UV for GaN films grown by the chloride transport method.[6,7] However, our measurement indicates that the deep exponential tail extends all the way to the infrared where transmission measurement would require much thicker samples. For sample 511, an additional steeper region is observed near the direct gap energy at 3.4 eV, with an E_0 of about 50 meV.

The absorption coefficient is proportional to the product of the densities of initial and final states integrated over all possible transitions for a given $h\nu$.[8] Hence, we propose the density of states distribution for *n*-type and *p*-type films as shown in Figs. 3(a) and 3(b), respectively. For *n*-type GaN, the equilibrium Fermi level at room temperature is close to the conduction band edge E_c. The dominant optical transition for the subband gap optical absorption (for $h\nu<3.4$ eV) in *n*-type GaN is from the valence band tail to the conduction

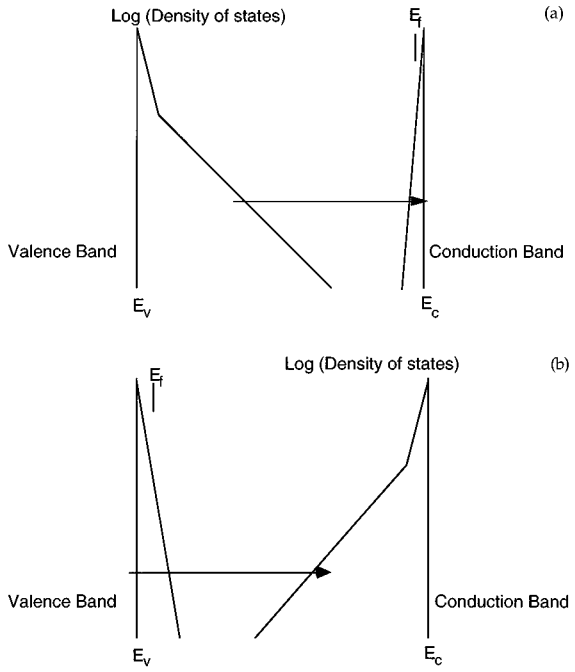

FIG. 3. Schematic density of states distribution in *n*-type GaN (a) and *p*-type GaN (b). The states between E_c and E_v are assumed to be localized states. The arrows represent schematically the dominant optical transitions for subband gap light absorption (for $h\nu<3.4$ eV).

band, and the measured PC tail is attributable to the valence band tail. Similarly, the measured PC tail of *p*-type GaN film is attributable to the conduction band tail [Fig. 3(b)]. Regarding the measured steep and gradual tailing for the undoped *n*-type GaN, we suggest that there are two exponential tails, an abrupt tail very close to the band edges and a gradual tail deeper into the gap. The abrupt tail may reflect the usual Urbach edge, arising from perturbations of the band structure by Coulomb potential of ionized impurities[9] and by local stresses.[10] The deep gradual tail is tentatively attributed to defect states. For the *p*-type sample AA1, Fig. 2 shows a flat region at $0.7\ \text{eV}<h\nu<1.4$ eV, indicating a minimum density of defects about 0.7 to 1.4 eV above the valence band edge.

We emphasize here that the PC data for the *n*-type and *p*-type conducting GaN (except PC data for the insulating GaN) cannot be interpreted based on a density of states distribution symmetric about the midgap of GaN. Figures 3(a) and 3(b) thus suggest that the conduction band tail grows and the valence band tail shrinks as Mg is incorporated into GaN. Based on this ''dynamic'' picture of Mg doping, the deep tail is expected to become steeper at some Mg doping level, as was indeed observed for the insulating *p*-type sample 214. This picture is further supported by the observation that the deep tailing seemed to disappear with Zn doping when the GaN films became insulating.[5]

The wide ranging absorption tail is quite unexpected for single crystalline materials. At present, we know little about the origin of the deep tail states. They may be largely related to the high growth temperature, the large stress arising from the lattice mismatch to the sapphire substrate, the large difference in the thermal expansion coefficients of GaN and sapphire, impurity incorporation, and impurity compensation. This tailing is much more profound than those of other crystalline semiconductors, and even more profound than in hydrogenated amorphous silicon.[11,12] Understanding their origin in order to eliminate the defect states will be an important endeavor in the near future for device development based on GaN films.

In summary, we measured the subband gap optical absorption in GaN films by photoconductivity spectroscopy. The PC response per incident photon decreases by more than four orders of magnitude with Mg doping. PC response is observed from near infrared to the near ultraviolet for all the MOCVD-grown GaN films on sapphire. Mg doping seems to generate states in the conduction band tail and to eliminate states from the valence band tail. For the higher quality undoped sample, an additional steeper region is observed near the direct gap energy, with an Urbach energy E_0 of about 50 meV. Thus, present-day GaN films appear ''dirty'' in the forbidden gap. Future work should reduce the density of undesired defect states.

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